

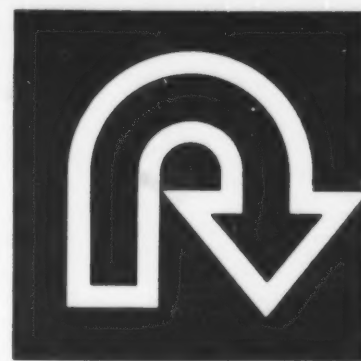
**FEDERAL/PROVINCIAL
RESEARCH AND MONITORING
COORDINATING COMMITTEE (RMCC)**

**DEVELOPMENT OF A NATIONAL
NITROGEN OXIDES (NO_x) AND
VOLATILE ORGANIC COMPOUNDS
(VOC) MANAGEMENT PLAN
FOR CANADA**

TECHNICAL ANNEX ON:

- I THE STATE OF THE ENVIRONMENT**
- II THE STATE OF ATMOSPHERIC
CHEMISTRY AND IMPLICATIONS
FOR CONTROL**
- III TRANSBOUNDARY FLOWS**

SPRING 1989



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Canada

Federal/Provincial
Research and Monitoring
Coordinating Committee (RMCC)

Development of a National
Nitrogen Oxides (NO_x) and
Volatile Organic Compounds
(VOC) Management Plan
For Canada

Technical Annex on:

- I The State of the Environment
- II The State of Atmospheric Chemistry
and Implications for Control
- III Transboundary Flows

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Secretariat of the Changing Atmosphere
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4905 Dufferin Street
Downsview, Ontario
Canada M3H 5T4

Phone: (416) 739-4645/4646

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Further Management of Emissions of Nitrogen Oxides
and Volatile Organic Compounds in Canada

Technical Annex

INTRODUCTION

In October 1988, the federal and provincial environment ministers requested that a comprehensive national plan be developed to further manage nitrogen oxides (NO_x) and volatile organic compound (VOC) emissions in Canada. The production^x of the plan is being coordinated by the Federal/Provincial LRTAP Steering Committee.

This technical annex has been prepared by the Federal/Provincial Research and Monitoring Coordinating Committee (RMCC) at the request of the LRTAP Steering Committee. The annex is divided into three sections.

The first section considers the state of the environment, including the effects of nitrogen-related compounds on the environment, existing environmental targets developed to protect human health and vegetation, and observed concentrations and deposition levels in Canada. The four pollutant problems of concern are: 1) nitrogen dioxide (NO_2) concentrations in urban areas; 2) tropospheric (ground-level) ozone (O_3) in both urban and rural areas; 3) the acidifying effects of nitric acid and ammonia; 4) nitrous oxide (N_2O) concentrations in the atmosphere. Ground-level ozone is the principal NO_x and VOC related air quality problem in many areas of Canada.

Section two describes the state of knowledge of atmospheric chemistry and implications for the control of ozone.

Section three discusses the transboundary contribution to the NO_x and VOC problem in Canada.



SECTION I - STATE OF THE ENVIRONMENT

NITROGEN DIOXIDE

Effects

Nitrogen dioxide is an orange-brown coloured gas with a characteristic pungent odour that can be detected at concentrations as low as .12 ppm (National Academy of Sciences, 1977). NO_2 is the only nitrogen oxide that is considered potentially phytotoxic within the range of ambient air concentrations (Legge and Crowther, 1987). Under high light intensities, about 6 ppm of NO_2 for two hours are required to injure sensitive plant species such as bean, tomato and cucumber. Low light intensity increases sensitivity of plants with injury developing after exposure to 2.5 to 3.0 ppm for two hours. NO_2 can injure the same plants as ozone and at the same time within the leaf tissue. Injury symptoms are, however, generally different. Long term exposure to NO_2 (0.25 ppm) can cause reductions in growth and yield.

Ambient NO_2 concentrations rarely reach the injury threshold for NO_x alone (see Table 1). Thus, recent terrestrial research on NO_2 has focused on the effects of mixtures of two or more phytotoxic gases. Synergistic (more than additive), additive and antagonistic (less than additive) effects on injury expression, growth and yield have been identified. The injury threshold for NO_2 falls to approximately 0.05 to 0.10 ppm after four hours when the exposure combines NO_2 with either or both ozone and SO_2 in at least equal concentrations (Reinhart, 1984).

NO_2 is a lung irritant which can produce pulmonary edema at very high concentrations (MOI, 1983). Increases in airway resistance have been found in healthy humans after 1 to 15 minutes of exposure to NO_2 concentrations ranging from 1.6 to 2.5 ppm (Von Nieding, 1973). Short and long-term exposure to high concentrations of NO_2 can enhance susceptibility to respiratory infections (MOI, 1983). However, concentrations of NO_2 in Canadian cities are generally well below the levels at which adverse effects on human health occur (see below).

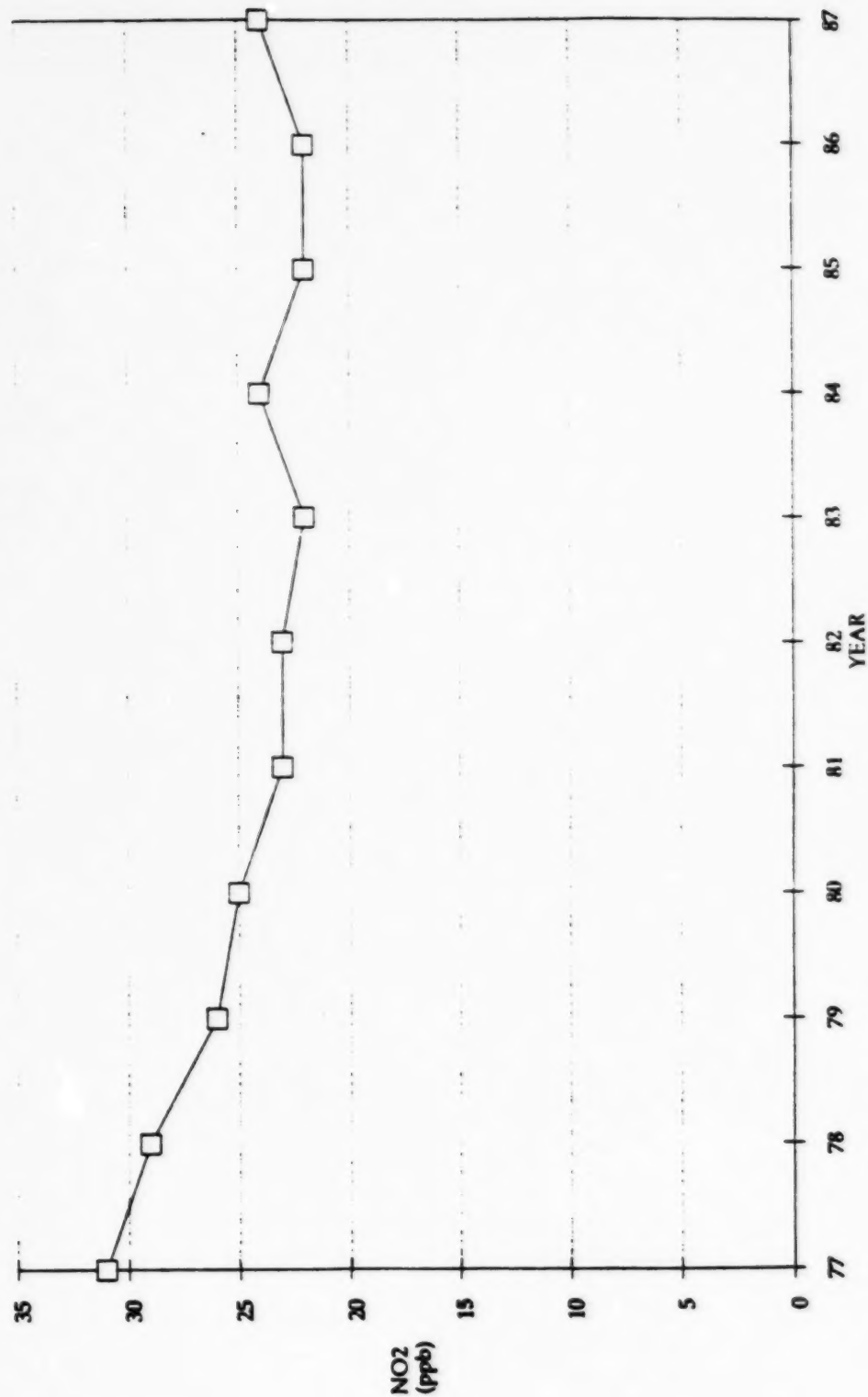
Objectives and Observed Concentrations

Canada has established National Ambient Air Quality objectives for NO_2 and a number of other pollutants including ozone. Details on the rationale behind these objectives are found in the Technical Annex Report No. 1. The "maximum acceptable level" has been developed to protect human health as well as visibility, animals, soil, water and vegetation. The maximum acceptable levels for NO_2 for exposure periods of 1-hour, 24-hours, and 1-year are shown in Table 1.

The composite average of nitrogen dioxide annual means from the National Air Pollution Surveillance (NAPS) monitoring stations is shown in Figure 1 for the period 1977-1987 (Dann, 1989a). The composite averages have been well below the maximum acceptable annual level of .05 ppm and since 1978 have been below the

FIGURE 1

COMPOSITE AVERAGE OF NAPS STATIONS ANNUAL MEAN
NO₂ CONCENTRATIONS (ppb) (DANN, 1989a)



maximum desirable level of .03 ppm. Between 1977 and 1981 there was a steady decrease in the composite average and since then there has been little change. Further reductions are expected to occur, in the short term, as a result of new federal motor vehicle emission standards.

In 1987, sites in Montreal and St. Catherines exceeded the 24-hour maximum acceptable level (on 14 and 15 occasions respectively) and sites in Toronto, Sarnia and St. Catherines exceeded the 1-hour maximum acceptable level (once, each). Over the past five years cities in British Columbia, Alberta, Saskatchewan, Ontario and Quebec have exceeded the 1-hour or 24-hour maximum acceptable levels on occasion (Dann, 1989a).

Critical levels have been established under the Economic Commission for Europe (ECE) for the Convention on Long-range Transboundary Air Pollution (U.N. ECE, 1988). A 1-hour average of 800 ug/m^3 (.40 ppm) NO_2 was proposed to protect vegetation. This level is twice the Canadian maximum acceptable level. In most ECE countries, ambient NO_2 concentrations have not been shown to produce visible injury to vegetation. For this reason, the ECE annual critical level for NO_x considers the effects of NO_2 in combination with sulphur dioxide and ozone (see Table 1).

OZONE

Effects

Ozone concentrations are highest during hot, sunny summer days because its formation is enhanced under these conditions. Each summer, approximately one half of Canada's population is exposed to ozone concentrations which are known to have health effects.

Ozone produces eye, nose and throat irritation at levels as low as .01 ppm (Concord Scientific Corporation, 1984).

High ozone concentrations can cause immediate short-term changes in lung function and increased respiratory symptoms. Koren et al (1989) has found that ozone levels as low as .08 ppm resulted in increased levels of inflammatory cells in subjects exposed for 6 hours. Healthy exercising individuals have been shown to experience decreases in lung function and increased respiratory symptoms during prolonged periods of exposure to ozone at concentrations as low as .12 ppm. Exercising children and adults have experienced a temporary reduction in lung function after 1-2 hours of ozone in the range of .12-.16 ppm. Pronounced symptoms such as cough and pain or deep breathing are observed in some adults exercising heavily under conditions of ozone of over .18 ppm.

There is increasing concern about the long-term effects of ozone. Ozone is known to damage the tissues lining the airways of the lung and is suspected of playing a role in the long-term development of chronic lung diseases (OTA, 1988).

In 1983, Bates and Sizto published the results of a study in which they found a significant relationship between excess hospital respiratory admissions and ozone, SO_2 and temperature, with a lag-time of 24-48 hours, during the summer months of 1974 and 1976-78. Bates and Sizto (1989) have recently examined hospital admissions for acute respiratory diseases during June 1983, a period during which there was an exceptional number of ozone episodes. There was no demonstrable excess in hospital admissions in June 1983 compared to admissions during the same period for several previous years. It was concluded that "probably neither ozone nor SO_4 alone is responsible for the observed association with acute respiratory admissions, but that either some unmeasured species (of which H_2SO_4 is the strongest candidate), or some pattern of sequential or cumulative exposure is responsible for the observed morbidity" (Bates and Sizto 1989: 69).

The effects of ozone on vegetation have been well-documented. Most of the Canadian research has focused on ozone injury to crops in southern Ontario. Ozone sensitive crops include beans, tomatoes, tobacco, potatoes, corn, soybeans and wheat. Farmers in Ontario could benefit by \$15-23 million per year if ozone concentrations were reduced to a seasonal mean of 30 ppb (7 hour mean) (Ontario Ministry of the Environment, 1984).

The response of forest systems to elevated ozone concentrations is not well understood and difficult to quantify due to the physical size of the plant material and the impossibility of exposing trees to controlled concentrations of ozone over their long and complex growth cycle. Ozone is known to cause foliar injury and reduced growth rates in sensitive tree species (OTA, 1988). Exposure to ozone can also increase susceptibility to secondary stresses such as insects and disease. Ozone damage and forest decline has been well-documented in the Los Angeles Basin and other parts of California.

In Eastern Canada, a decline of hardwood species is occurring. However, the role of ozone and other factors such as climate, insect, disease and other pollutants in the decline is not clear.

Objectives, Critical Levels and Observed Concentrations

Air quality objectives for ozone have been established in Canada (see Table 1). The maximum acceptable levels are expressed for exposure periods of 1-hour, 24-hours and one year. The ECE has proposed critical levels for exposure periods of 0.5, 1, 2, 4 and 8 hours (see Table 1). The one-hour ECE critical level of 0.075 ppm is only slightly more stringent than the Canadian one hour standard of 0.08 ppm.

An indication of the relative frequency of elevated ozone concentrations in the major Canadian cities is shown in Table 2. The Canadian maximum acceptable levels are often exceeded in the Vancouver Regional District and along the Windsor-Québec City Corridor.

Table 2. OZONE ONE HOUR MAXIMA AND HOURS >.08 ppm
FOR SELECTED URBAN SITES (1987 OR 1988)
(Adapted from Dann, 1989a)

City	Max. O ₃ (ppm)	Hrs>.08ppm	Year
Halifax	.122	3	1987
Montréal	.118	20	1987
Montréal	.121	15	1987
Windsor	.159	189	1988
London	.137	149	1988
Toronto (North York)	.177	157	1988
Oakville	.185	122	1988
Winnipeg	.080	0	1987
Saskatoon	.064	0	1987
Edmonton	.092	8	1987
Calgary	.084	2	1987
Vancouver	.167	34	1988
Vancouver (Pt. Coquitlam)	.213	31	1988

To prevent injury to sensitive vegetation during the growing season a maximum acceptable seasonal mean value (June to August, 7 hour mean, 9 a.m. - 4 p.m.) of .032 ppm for ozone has been proposed by the Canadian Federal/Provincial Advisory Committee on Air Quality. Growing season mean ozone concentrations for 1987 at selected rural sites are shown in Table 3. The proposed maximum acceptable growing season level was exceeded at most sites. The highest seasonal means were observed in Ontario.

The proposed growing season objective is comparable to the seasonal mean of .025 ppm recommended by the ECE (U.N. ECE, 1988).

Trends

On the national scale, peak ozone concentrations (composite average) have decreased over the last ten years in urban areas (see Figure 2). Decreases in average maximum ozone concentrations and in the number of hours greater than the maximum acceptable levels have been observed in the Greater Vancouver Regional District. In southern Ontario there has been little change in ozone levels. In 1988 southern Ontario experienced the greatest number of hours of concentrations exceeding the maximum acceptable levels since 1978.

There is evidence that background concentrations of ozone in the free troposphere (upper layer of the troposphere) of the northern hemisphere are increasing at a rate of 1-3 percent per year, due in part to anthropogenic emissions (Hov, 1988). This increase in free tropospheric ozone will have implications for future growing season mean ozone concentrations at rural sites in Canada.

In addition to having direct effects on plant life and health, ozone is known to be a global atmospheric warming agent.

NITRIC ACID AND ACIDIFICATION

Effects

Although nitrate is one of the main acidifying agents in wet and dry deposition, it does not appear to play a significant role in the long-term acidification of surface waters in Canada. The deposited nitrate is taken up by aquatic and terrestrial systems. Nitrogen is an essential plant nutrient which is often in short supply. The observed acidification of surface waters in Eastern Canada is attributed primarily to sulphate deposition (RMCC, 1986).

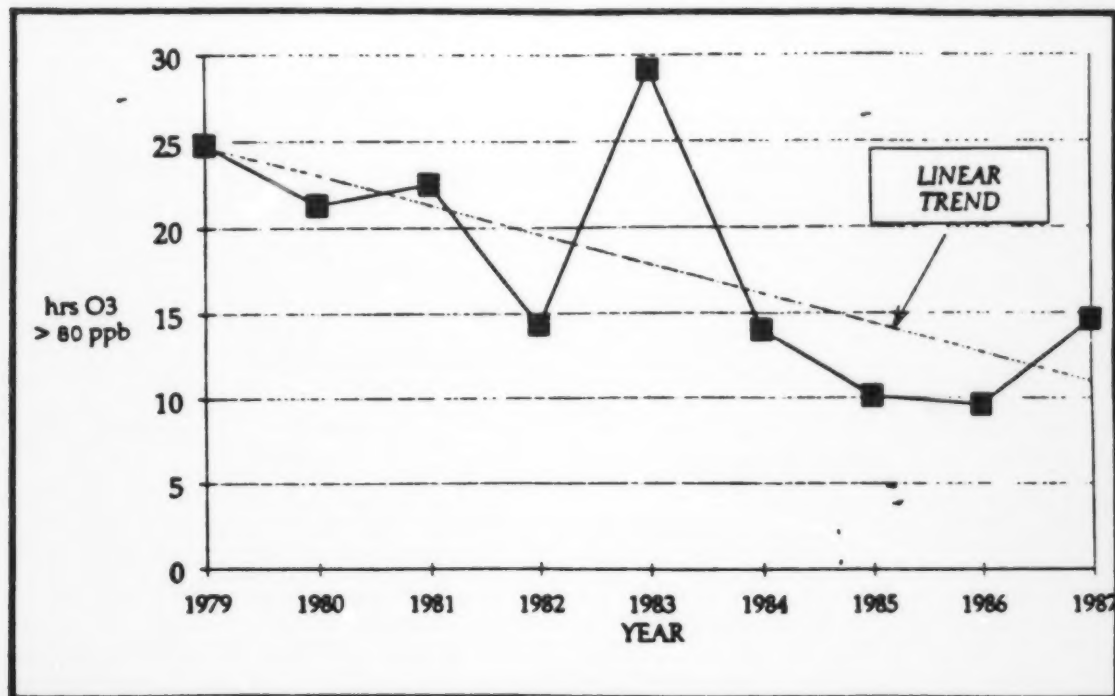
Dillon *et al.* (1989) has examined nitrogen retention in several forested catchments and lakes in Ontario. Retention of ammonium is comparable to retention of nitrate. Retention of total inorganic nitrate (ammonium plus nitrate) appears to be influenced more by the annual areal water discharge rate than by nitrate deposition. Dillon concludes that within the range of deposition observed at the study sites, changes in nitrogen loadings are not expected to alter the proportion of nitrogen retained and exported. However,

Table 3. OZONE CONCENTRATIONS AT SELECTED RURAL SITES (1987)
(Adapted from Dann, 1989a)

Location	Growing Season Avg. ppm ¹	Maximum 1 Hr Avg. ppm ²	Numbers of Hours Greater than .08ppm (160 ug/m ³)
Kejimikujik, N.S.	.031	.07	0
St. Etienne, P.Q.	.039	.11	11
St. Barnabé, P.Q.	.039	.12	12
Simcoe, Ont.	.049	.117	72
Mandaumin, Ont.	.048	.134	133
Huron Park, Ont.	.045	.121	89
Crossfield, Alta.	.037	.08	1
Abbotsford, B.C.	.033	.117	15
Seymour Lake, B.C.	.036	.099	12
Kelowna, B.C.	.038	.068	0

1. Recommended maximum acceptable growing season level is .032 ppm (64 ug/m³).
2. Maximum acceptable 1 hour objective is .08 ppm (160 ug/m³).

**FIGURE 2- COMPOSITE AVERAGE of the NUMBER of HOURS per SITE with
OZONE CONCENTRATIONS >80 PPB (45 SITES) (DANN, 1989a)**



changes in nitrogen loading will result in changes in the absolute amounts of inorganic nitrogen retained and exported, and therefore, increased nitrate deposition will result in higher nitrate concentrations and greater acidity in stream and lake waters.

Nitrate can potentially play an important role in short-term acidification, particularly during the springmelt, when acids accumulated in the snowpack over the winter are released in a few days. Dillon *et al.* (1989) has examined the chemistry of 15 headwater streams and lake outflows in three central Ontario catchments during springmelt in 1984-86. Alkalinity depressions occurred primarily as a result of base cation dilution by snowmelt water. As the degree of stream acidification increased, alkalinity depressions were associated with sulphate loadings. Nitrate did not contribute significantly to alkalinity depressions.

Excess nitrogen deposition can potentially harm forests. Nitrogen fertilization can alter winter hardening processes. In addition, vigorous growth stimulated by nitrogen can result in nutrient deficiencies if other nutrients are in short supply. These effects have not been observed in Canada. Canadian terrestrial systems generally benefit from nitrate deposition, at current loadings.

Objectives and Observed Nitrate Deposition

Canada has not established a critical load or deposition target for nitrate, comparable to the 20 kg/ha/year deposition target for wet sulphate developed for aquatic systems.

Critical load values for nitrogen have been developed by the ECE, see Table 1, (UN ECE, 1988). These critical load values are expressed in terms of total nitrogen which includes nitrate (NO_3) and ammonium (NH_4). The major sources of ammonium, which can also act as an acidifying agent, are livestock farming and agricultural practices. For forest soils, the critical load is assumed to occur when the biota on and in the soil, and the soil itself, are unable to absorb the deposited nitrogen. For forest soil systems with low productivity a critical load of 3-11 kg N ha/yr (wet and dry) has been recommended to protect surface waters. For forest soil systems with high productivity, a higher critical load of 7-20 kg/ha/yr is proposed (see Table 4). Critical loads have also been proposed for other ecosystems (see Table 5) and to protect sensitive biota (see Table 6). The applicability of these targets for Canada has not been evaluated.

Wet nitrate deposition (expressed as nitrogen), wet ammonium deposition (expressed as nitrogen) and total wet nitrogen deposition are shown in Figures 3-5. Total wet nitrogen deposition (nitrate and ammonium) in the Prairies for 1986 was less than 2 kg/ha/yr. Wet nitrate deposition (expressed as nitrogen) in B.C. in 1987 ranged from less than 1kg/ha/yr to 3kg/ha/yr. Estimates of dry deposition of nitrogen are uncertain in part because there are no rural measurements of NO_2 . Barrie *et al.* (1989) estimate that dry nitrogen deposition in Eastern Canada contributes 30-60 percent of the total nitrogen deposition.

Table 4. Critical N loads for production forests (kg N ha^{-1})*** on well-drained sites assuming whole tree harvest (U.N. ECE, 1988)

	N-accumulation in growth	Acceptable N-accumula- tion in soil	Leaching**	Critical N input**
Low productivity net N immobilisation	1 - 6	1 - 3	1 - 2	3 - 11
Low productivity net N mineralisation	1 - 6	-	-	0*
High productivity net N immobilisation	5 - 15	1 - 3	1 - 2	7 - 20
High productivity net N mineralisation	5 - 15	-	-	0*

* Any N input to declining systems will delay recovery

** Critical N input may approach weathering rate if sulphur load is low

*** Values can be converted into $\text{mol m}^{-2}\text{yr}^{-1}$ by dividing with 140

Table 5. Critical N loads for ecosystems varying in productivity ($\text{kg N ha}^{-1} \text{yr}^{-1}$) (U.N. ECE, 1988)

Ecosystem	Critical Load
Deciduous forests**	5 - 20*
Coniferous forests**	3 - 15*
Dwarf shrub vegetation	3 - 5***
Grassland (e.g. mesobrometum)	3 - 10***
Raised bog	3 - 5***

* In mature forest the critical load may approach 0

** Declining systems should approach 0

*** Without major removal of N by management

Table 6. Summary of biological consequences and critical loads (U.N. ECE, 1988)

System	Criteria	Estimated Critical Load kg N/ha-yr	Reference Country
Littoral communities	Shallow soft water communities sensitive to NH_4 when NO_3 is low, critical load as NH_4	3 - 7	Netherlands
Raised bogs	Sphagnum very sensitive to NO_3 (but less sensitive to NH_4). Response in a very short time due to toxicity, 5-10 kg due less than 1 year	-	Netherlands Great Britain
	Possible changes in flora, eg. increased growth of bushes and trees but other nutrients, eg. K, limit growth rather soon.	5 - 10	Sweden Great Britain Federal Republic of Germany
Heathlands	Reduced frost resistance of <i>Calluna</i>	5 - 20	Netherlands
	Changes in species comp., depends on weathering capacity. Low buffering soils	7 - 10	Netherlands
	Heath to grassland conversion (complete change)	> 20	Netherlands
	With intensive management (grazing + cyclical burning + topsoil removal), <i>Calluna</i> and <i>Erica</i> can be maintained	< 40	Netherlands
Coniferous forests	Nutrients imbalances due to high nitrogen input depends on Mg and Ca concentration and nitrification rate. Most sensitive systems.	10 - 12	Netherlands
	Changes in herbaceous flora towards nitrophilic species but critical load depends on uptake by trees and saturation	> 20	Netherlands
	Pine stands with management; positive growth response during 15 years with an annual fertilizer application as NH_4NO_3 up to 30 kg, but changes in ground flora		Sweden
Deciduous forests	Changes in herbaceous flora towards nitrophilic species	< 15	Sweden

FIGURE 3
NATCHEM DATA BASE - AQUATIC EFFECTS SUBGROUP PROJECT
WET N-NO3 DEPOSITION IN 1986 (KG/HA)

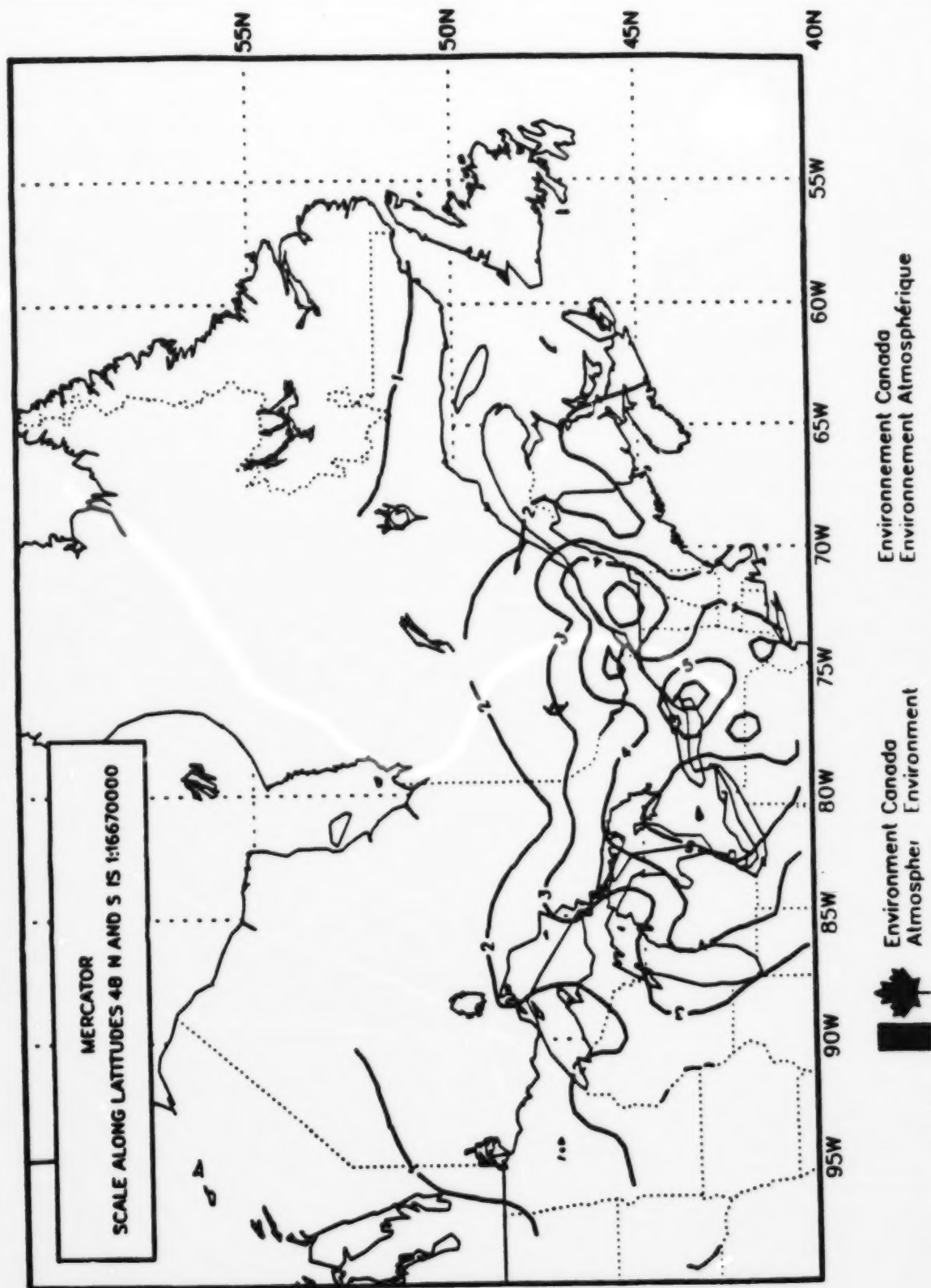


FIGURE 4
NATCHEM DATA BASE - AQUATIC EFFECTS SUBGROUP PROJECT
WET N-NH₄ DEPOSITION IN 1986 (KG/HA)

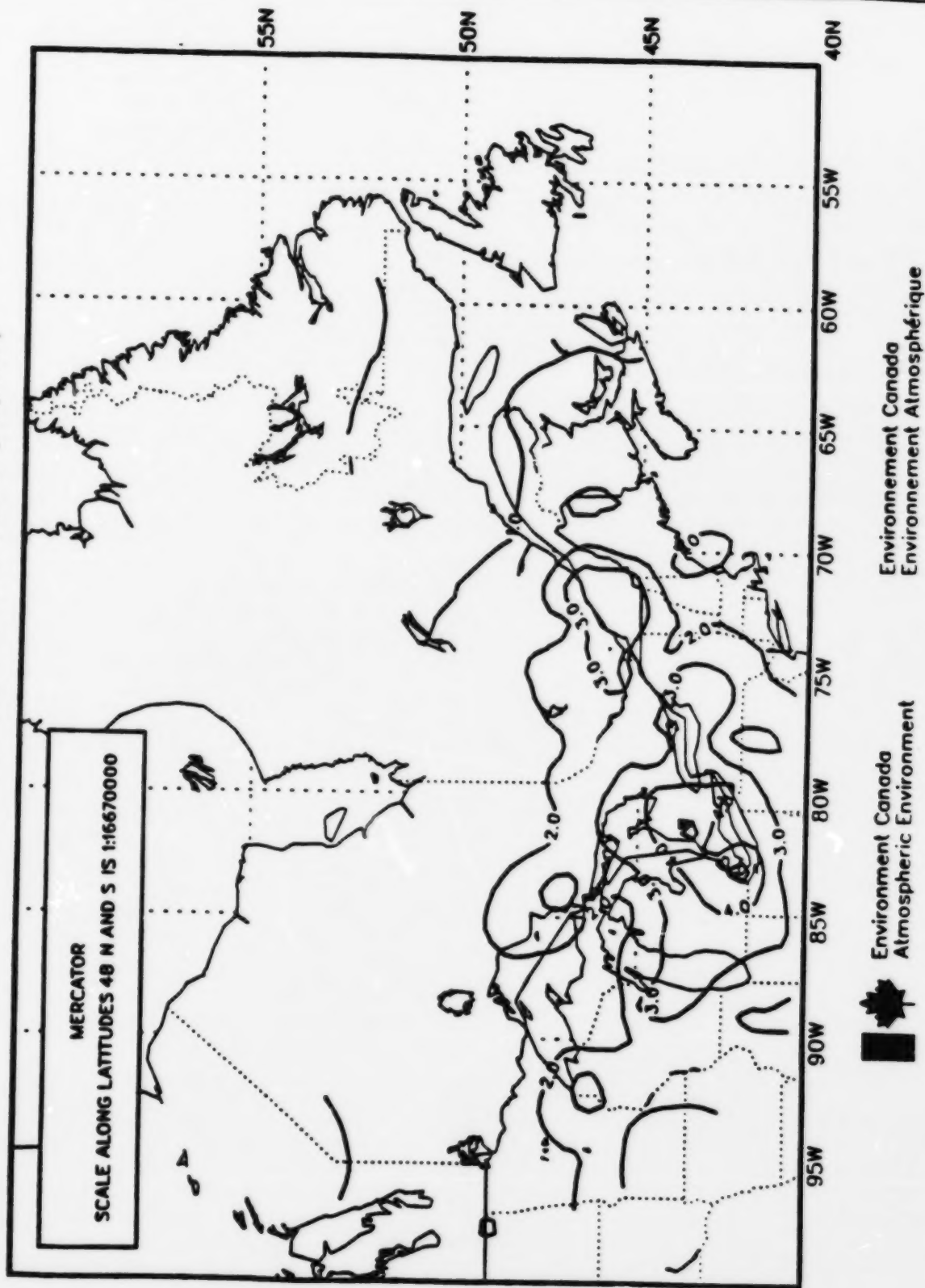
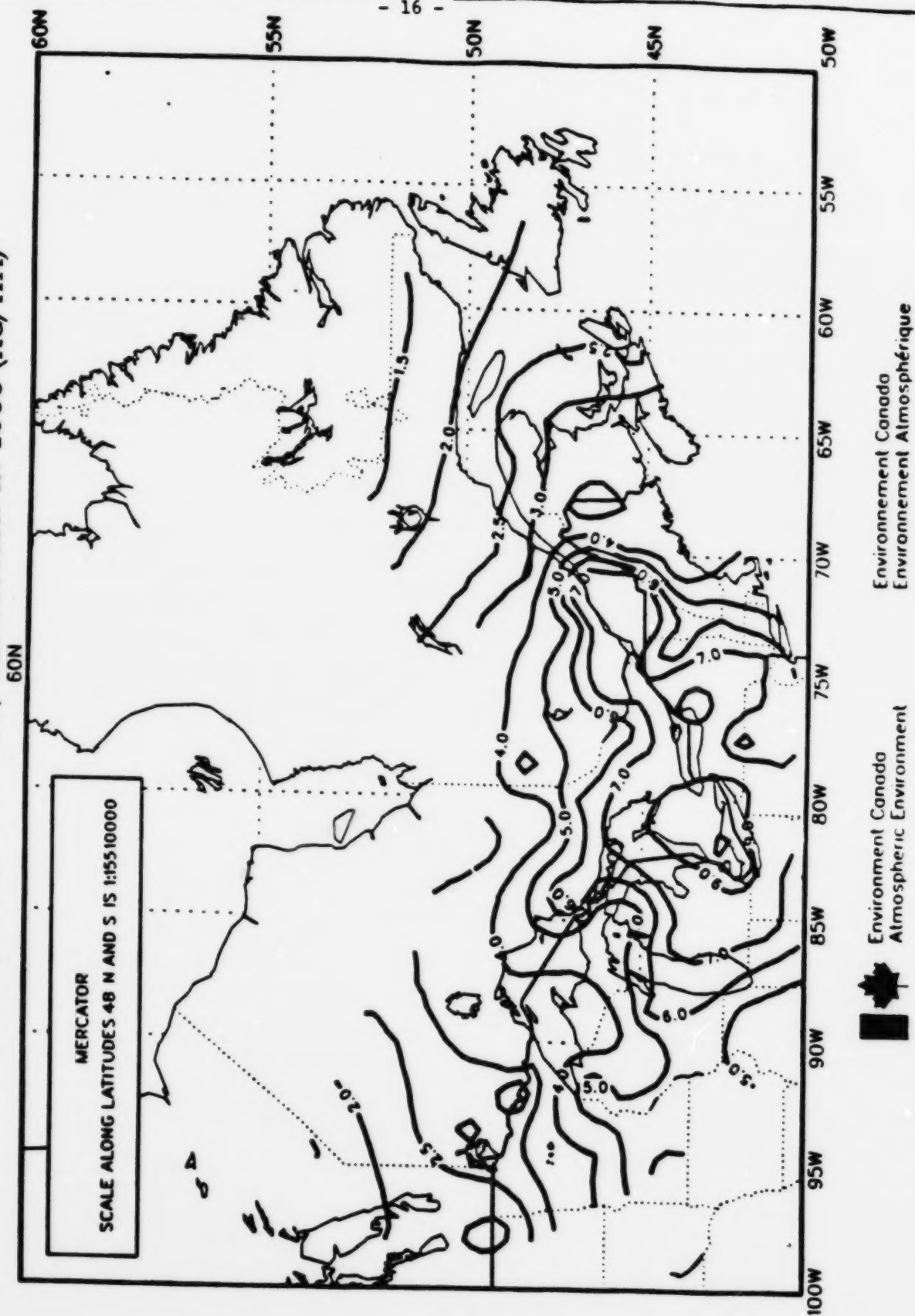


FIGURE 5
 NATCHEM DATABASE
 WET N-(N-NH4 + N-NO3) DEPOSITION IN 1986 (KG/HA)



NITROUS OXIDE

Nitrous oxide (N_2O) is known to be a global atmospheric warming agent and a stratospheric ozone depletion agent. Approximately one-third of total global N_2O emissions are anthropogenic, resulting mainly from fertilizer application and to a lesser extent from large stationary combustion sources. Mobile sources are not significant emitters of N_2O .

Nitrous oxide is estimated to contribute about 5% to global warming and will be of increasing concern from that perspective in the years ahead. Nitrous oxide would normally also contribute to stratospheric ozone depletion. However, in the present situation of elevated levels of chlorine compounds in the stratosphere (mainly due to chlorofluorocarbons), a situation that will prevail for decades, ozone depletion is slowed by increasing N_2O concentrations due to interference of the N_2O with the chlorine-catalyzed destruction of ozone.

SECTION II - STATE OF KNOWLEDGE OF ATMOSPHERIC CHEMISTRY AND IMPLICATIONS FOR CONTROL

Nitrogen Chemistry

The chemistry of nitrogen compounds in polluted atmospheres is complex. A summary of the reactions that occur in the gas-phase is shown in Figure 6 (MOI, 1982).

Nitrogen oxides are formed during high temperature combustion processes. Most of the nitrogen oxides emitted into the atmosphere are in the form of NO. NO₂ emissions at combustion sources are generally less than 10 percent (U.S. EPA, 1982). Once in the atmosphere, NO takes part in the central loop of reactions shown in Figure 6 which can ultimately lead to the formation of ozone (O₃), nitric acid (HNO₃), hydrogen peroxide (H₂O₂), and peroxyacetyl nitrate (PAN).

Volatile organic compounds (VOCs), primarily non-methane hydrocarbons play an important role in the cycle. In the presence of sunlight, free radical precursors such as ozone, formaldehyde and nitrous acid, decompose to produce radical species such as OH, HO₂, and RO₂. VOCs are rapidly decomposed by these highly reactive radical species, producing more radicals. The peroxy radical species HO₂ and RO₂ can react with NO to form NO₂ and hydroxyl/alkoxyl radical species which can be further oxidized to form peroxy radicals or may react with VOCs.

Non-methane hydrocarbons important in the production of NO₂ and ultimately ozone are shown in Table 7 (Dann, 1989). There are four main chemical classes: 1) alkanes or paraffins; 2) alkenes or olefins; 3) aromatics; and 4) aldehydes and ketones. The most chemically reactive compounds are the alkenes which are emitted primarily from the transportation sector but also by forests. The alkanes are the most abundant species in urban ambient air.

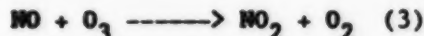
The formation of ozone in the troposphere (see left side of the Figure 6) is primarily controlled by three reactions. In the first reaction, NO₂, in the presence of sunlight, dissociates to form nitric oxide and a single oxygen atom.



The single oxygen atom reacts with atmospheric oxygen to form O₃.



A third reaction acts continuously to destroy ozone and regenerate NO₂.



The steady-state concentration of ozone at a particular site depends on the following equation (Dodge, 1987):

$$[\text{O}_3] = K_1 \times ([\text{NO}_2]/[\text{NO}]) \times \text{Constant},$$

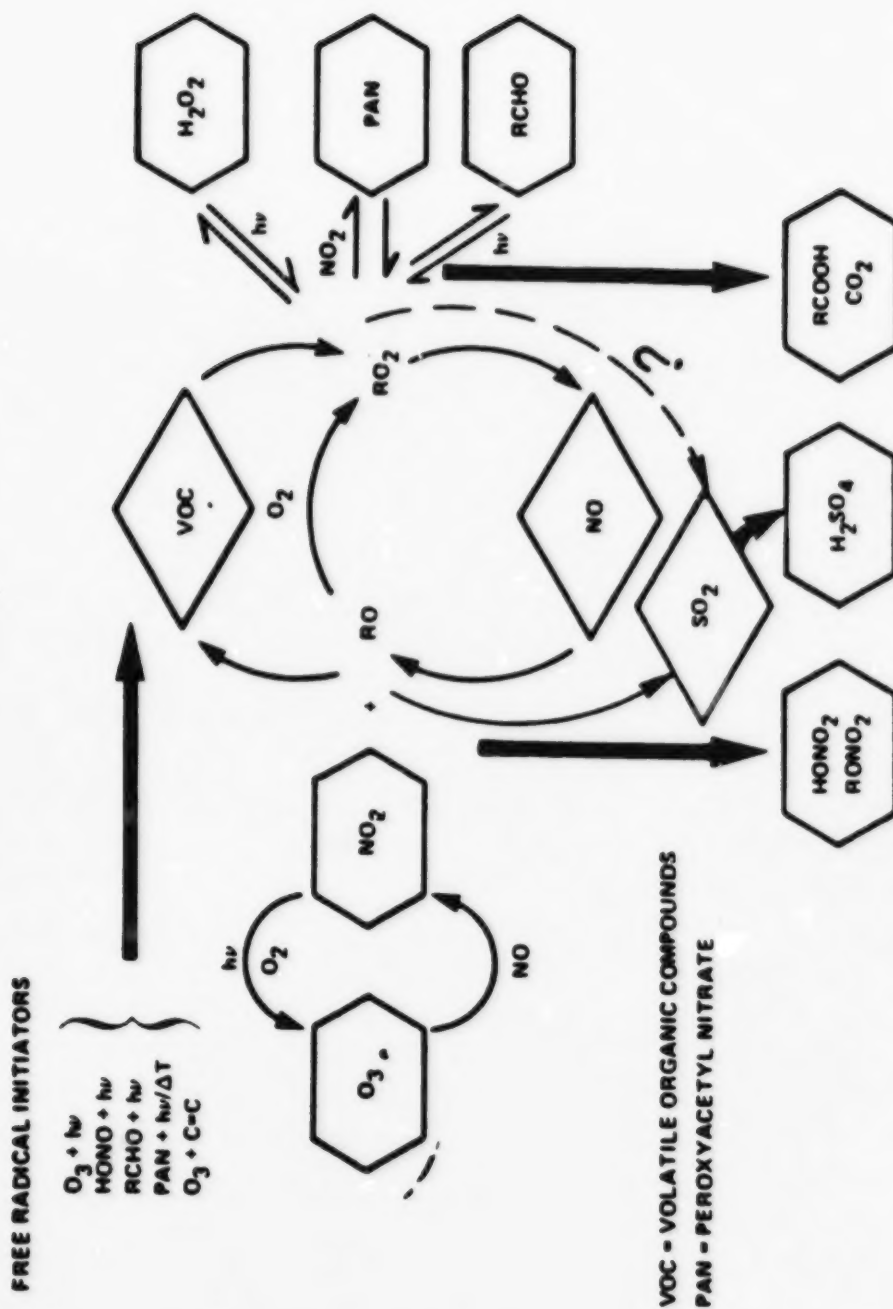


FIGURE 6 Schematic of the polluted atmosphere gas-phase photooxidation cycle

**TABLE 7 - IMPORTANT VOLATILE ORGANIC COMPOUND CLASSES
and SPECIES in AMBIENT AIR re OXIDANTS ISSUE (DANN, 1989a)**

Category	Representative Species	Representative Reactivity Coefficient $10^3 (k_{OH})$ (ppm ⁻¹ min ⁻¹)	Typical Fraction of Urban Ambient Air Sample*
1. Alkanes (Paraffins)	Ethane 2,3-Dimethylbutane n-Hexane	0.40 9.2 8.3	40-70%
2. Alkenes (Olefins)	Ethylene cis-2-Butene Isoprene α -pinene	12.6 46.5 149 78.7	5-12%
3. Aromatics	Benzene m-Xylene Ethylbenzene 1,2,4-Trimethylbenzene	1.9 36.3 11.1 63.3	20-40%
4. Aldehydes & Ketones (Carbonyls)	Formaldehyde Acetaldehyde	13.3 23.7	1-5%

* Excluding Methane

where K_1 is the rate of photolysis of NO_2 . When the ratio of NO_2 to NO is low there is little build up of ozone. However, when VOCs and sunlight are present in the atmosphere NO is converted into NO_2 , which lead to an increase in the NO_2 to NO ratio, and hence results in increased O_3 concentrations.

NOx Emissions

Nitrogen oxide emissions are produced primarily as a result of the combustion of fuel in mobile sources (the transportation sector) and in stationary sources. Canadian NO_x emission data for 1985 is presented in the Technical Annex-Report No. 2.1. ^xProjections of NO_x emissions for 1985-2005 are found in the Technical Annex-Report No. 2.2.

VOCs Emissions

There are both anthropogenic and natural sources of VOCs. Anthropogenic VOCs are emitted from the transportation sector, solvent use, fuel marketing and industrial processes. The Canadian VOC emissions inventory for 1985 is shown in the Technical Annex-Report No. 3.1 and projections for 1985-2005 are found in Report No. 3.2.

Natural sources of VOCs included gas and oil fields, volcanoes, vegetation and bacterial processes. The most important natural VOC is isoprene. Deciduous trees emit isoprene during daylight at a rate that increases rapidly with rises in temperature (Abelson, 1988). Evergreens emit pinene, another important natural VOC, on a 24-hour basis although emissions increase with high temperatures (Abelson, 1988).

Inventories of natural VOC emissions have been developed for use in atmospheric models, however, the accuracy of these inventories is questionable. Ambient measurement programs at 19 Canadian urban sites has shown that isoprene typically accounts for less than 2 percent of total carbon (Dann, 1989b). Isoprene accounted for 1.5 to 4 percent of the total carbon at 3 rural sites in Ontario (Dann, 1989b).

Factors Controlling the Rate of Ozone Production and Implications for Control Strategies

The rate of conversion of NO to NO_2 is dependent upon the VOC/NO_x ratio, hence, "the effectiveness of a proposed (ozone) control measure depends critically on the ratio of VOC and NO_x precursors" (Dodge, 1987: 56). In areas where the VOC/NO_x ratio (VOCs measured in ppb of carbon by volume, NO_x in ppb by volume) is low (less than 5:1) the system is limited by the concentration of VOCs. The appropriate control strategy in such areas is to reduce the limiting reactant, i.e. VOCs. In areas with high VOC/NO_x ratios the system is NO_x limited and ozone levels can best be controlled^x by reducing NO_x . In the intermediate range where the ratio is between 10:1 and 20:1 control of either VOCs or NO_x will reduce ozone levels. These strategies are summarized in Table 8. ^x

Table 8. Appropriate Ozone Control Strategies Under Varying VOC/NO_x Ratios

Ratio	Control Strategy
Less than 5:1	VOC Control
10:1 to 20:1	Either VOC or NO _x Control
Greater than 20:1	NO _x Control

The isopleth diagrams shown in Figures 7, 8 and 9 further illustrate the relationship between emission control strategies and VOC/NO_x ratios (Dodge, 1987). These isopleth diagrams were generated by Empirical Kinetics Modelling Approach (EKMA).

The effect of reducing either VOC or NO_x by 25 percent at low VOC/NO_x ratios is shown in Figure 7. At Point A the ozone concentration is .24 ppm and the VOC/NO_x ratio is approximately 3:1. Reducing VOCs by 25 percent (Point B) results in a decrease in the peak ozone concentration to .12 ppm. Reducing NO_x concentrations by 25 percent results in an increase in peak ozone concentration to a level of .20 ppm (see Point C).

Figure 8 demonstrates the effect of reducing VOC or NO_x emissions by 25 percent under conditions of high VOC/NO_x ratios. At Point A the ozone concentration is .20 ppm and the VOC/NO_x ratio is approximately 30:1. A 25 percent reduction in NO_x results in a reduction of O₃ concentration to .17 ppm (Point B) while a 25 percent reduction in VOCs does not change the ozone concentration.

Figure 9 illustrates the effect of reducing NO_x or VOCs by 25 percent at an intermediate VOC/NO_x ratio. Both options result in similar reductions in ozone levels.

Because these isopleth were generated by EKMA they are most applicable to isolated urban areas. Rural situations, multiday urban episodes, and episodes where the influx of ozone and/or ozone precursors is significant may have different control requirements. As well, Sillman et al (1988) have observed that the absolute concentrations of VOC and NO_x are important in the design of control strategies in addition to the VOC/NO_x ratio.

VOC/NO_x Ratios

There have been technical problems associated with monitoring VOC concentrations in ambient air. As a consequence, the Canadian data set is incomplete and there are few long term data available for specific sites. Recent advances have resulted in standardized measurement techniques and monitoring programs have now been established in Halifax, Montreal, Toronto, Hamilton, Windsor, Walpole Island, Sarnia and Vancouver (Dann, 1989).

There are very few VOC data for rural areas of Canada.

NO₂ is monitored at 74 urban sites in Canada (Dann, 1989). Nitric oxide (NO) and total nitrogen oxides (NO_x) concentrations are also monitored at most of these sites. There are very few rural sites which monitor NO₂ and NO_x because most commercial instrumentation is not sensitive enough to measure the lower concentrations present at many rural sites (Dann, 1989).

FIGURE 7

EFFECT ON OZONE CONCENTRATIONS (ppm) OF REDUCING VOC OR NO_x BY 25% AT LOW VOC/NO_x RATIOS (DODGE, 1987)

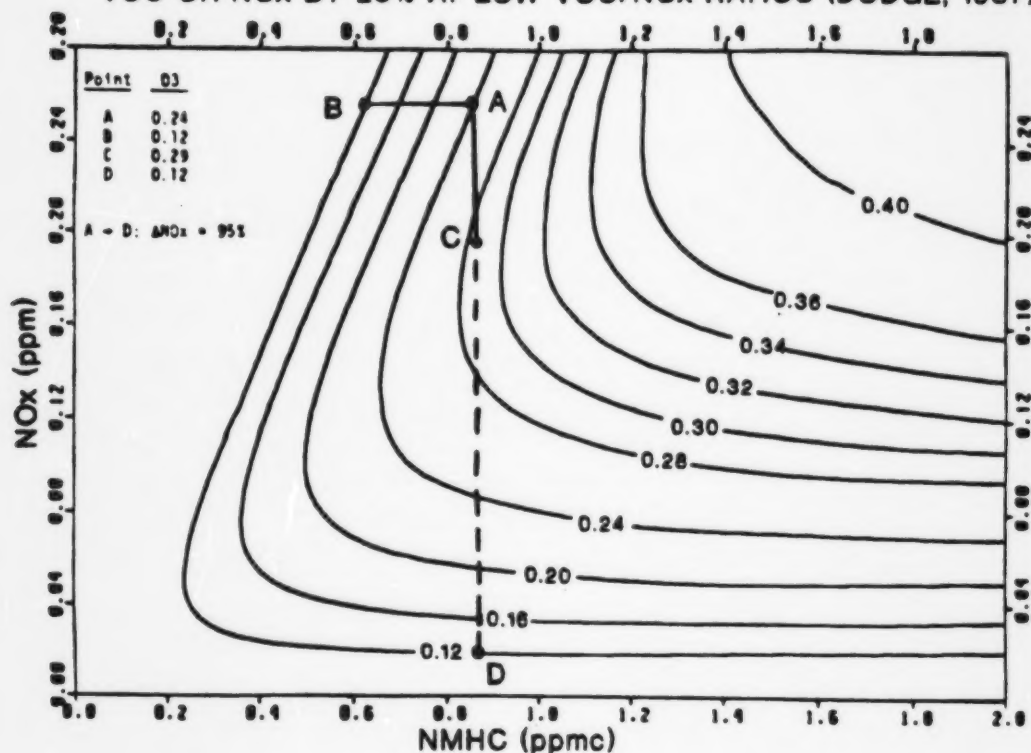


FIGURE 8

EFFECT ON OZONE CONCENTRATIONS (ppm) OF REDUCING VOC OR NO_x BY 25% AT HIGH VOC/NO_x RATIOS (DODGE, 1987)

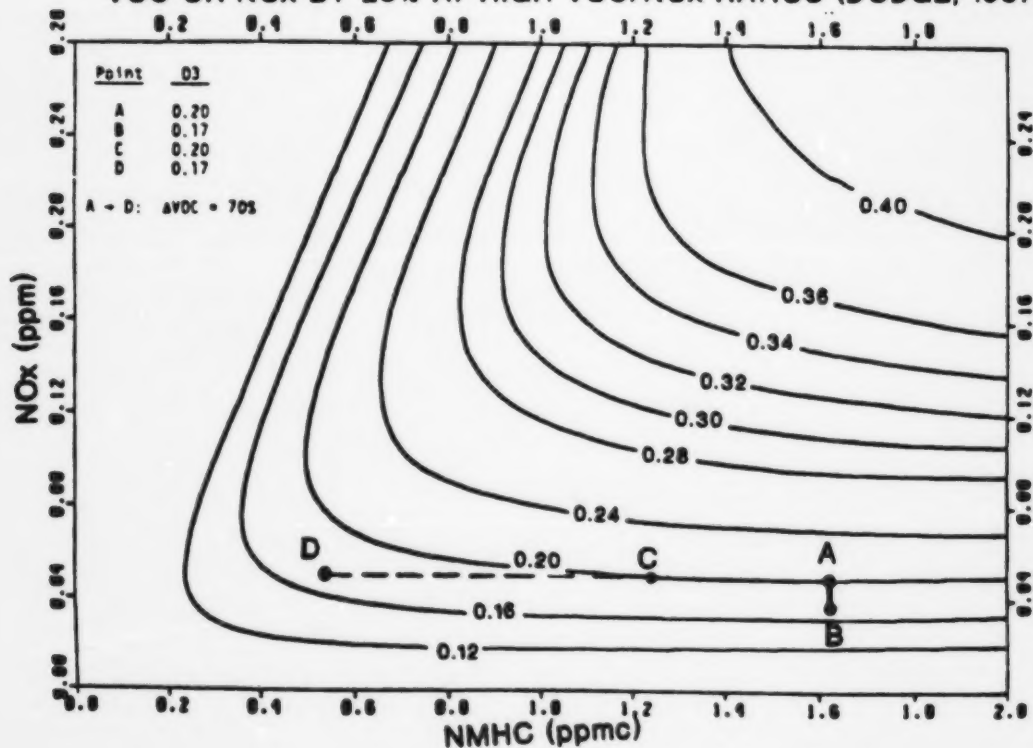
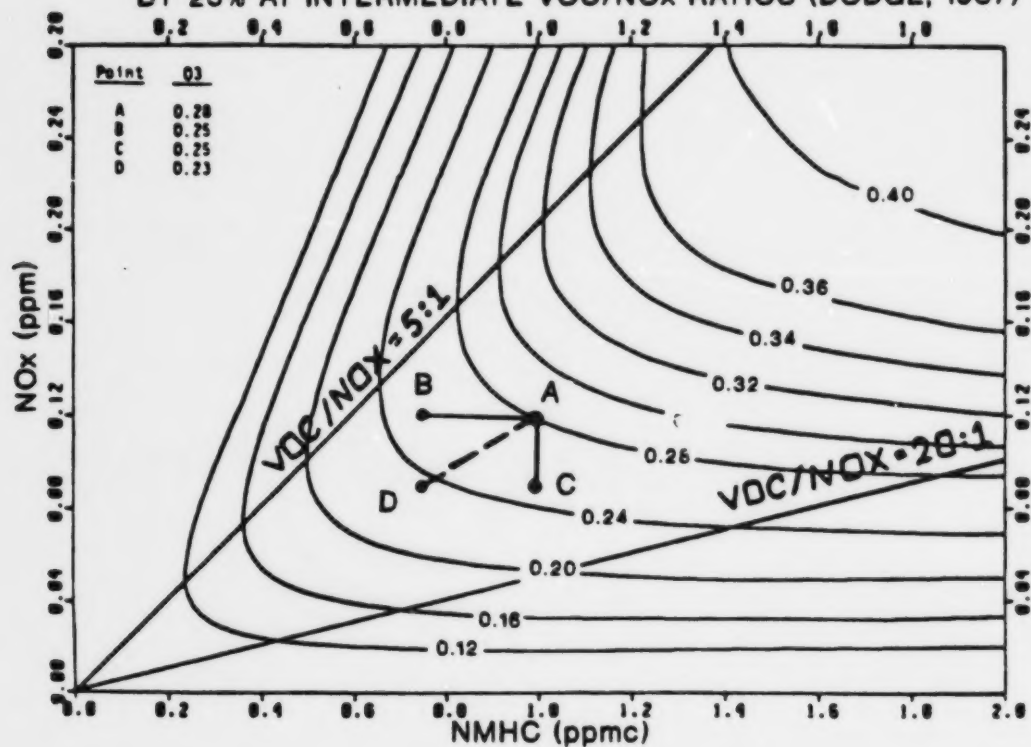


FIGURE 9
EFFECT ON OZONE CONCENTRATIONS (ppm) OF REDUCING VOC OR NO_x
BY 25% AT INTERMEDIATE VOC/NO_x RATIOS (DODGE, 1987)



There are six sites in Canada where there are sufficient although limited VOC data and nearby NO_x monitors to calculate VOC/NO_x ratios. Ratios for these sites are shown in Table 9. All of these urban sites, except Stouffville, a more rural site, have median ratios in the intermediate range, indicating that either NO_x or VOC control would be equally effective in reducing ozone concentrations.

Atmospheric Models

A variety of atmospheric models are available to assist decision-makers in evaluating control strategies for ozone (see Seinfeld, 1988; Wolff et al., 1988; and CSC, 1984). Some of these models are suitable for urban areas while others have been developed for regional scale applications. A number of models which may be useful for assessing control options for Canada will be briefly described below.

i) Empirical Kinetics Modelling Approach (EKMA)

EKMA is a city-specific trajectory-based model which has been used by the U.S. Environmental Protection Agency to develop State Implementation Plans to achieve National Ambient Air Quality Standards for ozone. It is easy to use and has only modest data requirements. The model uses input data on morning concentrations of VOCs and NO_x, emissions of VOCs and NO_x during the day, meteorological conditions and the reactivity of different VOC mixtures. The model predicts the relative reduction in precursors required to reduce peak ozone concentrations to a specified standard.

The EKMA method is appropriate for application to areas that have "a clearly definable urban core" and "a simple travel path to the point of downwind ozone maxima" (Seinfeld, 1988:619). Seinfeld (1988:619) further notes that the method should not be used for:

- 1) the rural ozone problem;
- 2) situation in which transported ozone and/or precursors are clearly dominant, such as multiday transport situations;
- 3) cases in which the maximum ozone concentration occurs at night or in the early morning; and
- 4) the development of control strategies for single or small groups of emission sources.

ii) Urban Airshed Model (UAM)

UAM was developed and remains the property of Systems Applications Inc. of California. It is a grid-based model which uses 30 x 30 squares, with sides of two miles each. Up to seven vertical layers can be incorporated into the model. The model uses the advanced Carbon Bond IV chemical mechanism and takes account of the reactivity of five different classes of VOCs.

UAM has been applied to urban areas in the northeastern United States, California, Great Britain, southern Europe and the Netherlands. The British Columbia government is currently considering the use of the model in Greater Vancouver Regional District.

Table 9. Ratios of Non-methane VOCs to NO_x

City	VOC/NO _x			Sampling Dates	No. of Samples	Reference
	Med.	Max.	Min.			
Toronto (Queen's Park)	9.5	12.7	8.3	July-Oct. 1987	9	Dann, 1989
Stouffville	26.0	34.1	10.9	July-Oct. 1987	16	Dann, 1989
Sarnia	15.1	76.5	3.4	-	-	Reid/Wong, 1988
Windsor	9.7	41.6	4.1	July-Dec. 1987	20	Dann, 1989
Vancouver T18	11.8	16.1	4.0	Aug.-Oct. 1987	9	Dann, 1989
Vancouver T22	15.1	63.8	3.5	Aug.-Oct. 1987	23	Dann, 1989

111) Acid Deposition and Oxidant Model (ADOM)

ADOM has been developed cooperatively by the Ontario Ministry of the Environment, Environment Canada and the Federal Republic of Germany. It is a three dimensional Eulerian model with a grid size of 127 x 127 km. It was originally designed to simulate the transport, transportation and deposition of acidic compounds; however, it can also be used to provide information on the formation of ozone.

The model has been developed for eastern North America but also could be modified for use in the Prairies. It cannot adequately simulate the complex terrain in British Columbia and Alberta.

The model development phase of ADOM is now complete. A two-year field evaluation program is now underway.

ADOM has been used to investigate the effects of different emission control scenarios on ozone levels in Ontario during a severe episode. The results of this analysis are discussed below.

The U.S. Government has developed a very similar model, the Regional Acid Deposition Model (RADM). ADOM and RADM intercomparison studies have been initiated. The field evaluation for RADM is being done in cooperation with the Canadian ADOM field evaluation.

iv) Regional Oxidant Model (ROM)

ROM is a model which has been developed by the US EPA for application to the eastern states. The model covers a 1000 km by 1000 km domain. The model has much better resolution than ADOM or RADM as its horizontal grid spacing is 18 by 18 kilometers.

Effects of Emission Control Scenarios on Ozone Concentrations in Ontario

ADOM has been applied to a single nine day episode in June 1983 to assess the relative contributions of NO_x and VOC emissions from Ontario and the United States to high ozone levels in Ontario. During the episode, ozone concentrations were above 80 ppb at many sites in Ontario and the northeastern U.S. The results of the study are summarized in Kurtz et al. (1989).

The five emission reduction scenarios and their effects of ozone levels in Ontario are discussed below:

1) 100 percent reduction of NO_x emissions in Ontario

This scenario resulted in an average reduction of 12 percent in maximum ozone concentrations in southern Ontario, although the percent reduction varied in each grid cell and was as high as 30 percent at some days at certain sites. There was little effect on ozone concentrations in northern Ontario.

2) 100 percent reduction of anthropogenic VOC emissions in Ontario

The 100 percent VOC cut had very little effect on ozone concentrations in southern Ontario. There was no significant change in central and northern Ontario, due in part to the importance of natural VOC emissions.

3) 100 percent reduction in NO_x and anthropogenic VOC emissions in Ontario

The results of this scenario were very similar to scenario 1, indicating that ozone formation in Ontario during the episode was limited by NO_x. Indeed nearly all of the VOC/NO_x ratios calculated by the model for the episode were very high, well over the 20:1 ratio when NO_x becomes the limiting factor.

4) 50 percent reduction in NO_x emissions in the U.S.

The 50 percent reduction in U.S. NO_x emissions resulted in an average reduction of maximum ozone concentration in southern and central Ontario of 10 percent.

5) 50 percent reduction in anthropogenic VOC emissions in the U.S.

This scenario had very little effect on maximum ozone concentration in Ontario.

This preliminary study indicates that reductions of NO_x in Ontario and the U.S. would be more effective in lowering ozone levels, than reductions in anthropogenic VOC emissions. It should be cautioned that these results were obtained from a model that has not yet been validated.

Similar studies for other parts of eastern Canada could be undertaken using ADOM.

U.S. Experience

Control strategies in the U.S. aimed at compliance of the ozone standard have been largely unsuccessful. Over 60 major urban areas experienced ozone peaks above the 1 hour standard of 120 ppb over the last three years (Abelson, 1988). A variety of reasons for the failure to attain the standard have been suggested. These include: the emphasis of VOC emission control as opposed to NO_x control, the poor guidance from models in the past, inadequate inventories of anthropogenic and natural emissions, and inadequate State Implementation Plans (Wolff, 1988 and Lulis, 1989).

SECTION III - QUALITATIVE AND/OR QUANTITATIVE DESCRIPTIONS OF THE TRANSBOUNDARY FLOWS OF NO_x, VOCs AND OZONE

Nitrogen

The ability to model the long-range transport of nitrogen is much less advanced than it is for sulphur. However, Lagrangian-type models have been used to a limited extent to compute nitrogen budgets for North America.

One such model is the Advanced Statistical Trajectory Regional Air Pollution (ASTRAP) model produced by the Argonne National Laboratory in Illinois (Shannon, 1986). The model, which assumes linear atmospheric chemistry between emission and deposition, employs parameterization procedures similar to those used for the simulation of transport and deposition of sulphur, although with different rates. A deposition budget for nitrate (expressed as nitrogen) produced by the model is shown in Table 10. Approximately two-thirds (64 percent) of the nitrate deposition in Canada in 1980 resulted from U.S. sources. Canada contributed to 3 percent of the nitrate deposition in the U.S.

Preliminary budget calculations are also available from the AES-LRTAP model (Olson et al, 1988). The estimated N flux into eastern Canada from the U.S.A. is 1.0 million tonnes per year, approximately three times the eastern Canadian emissions. The estimated flux from eastern Canada to the U.S. is .5 million tonnes. The fraction of the total deposition over eastern Canada attributable to U.S. or Canadian sources has not yet been calculated. However, the current transboundary flux estimates strongly suggest that the largest contribution is from the U.S.

An analysis has been carried out of episodes producing the highest 5 percent of the airborne concentrations of NO₃ (nitric acid plus particulate nitrate) at the Atmospheric Environment Service (AES) monitoring sites in eastern Canada (Summers, 1987). Using the air mass trajectories associated with the episodes, together with the geographical distributions of NO_x emissions and an appropriate decay factor to account for losses along the path, empirical source-receptor relationships have been generated. It is estimated that the U.S. NO_x source contribution to the highest airborne nitrate and nitric acid ranged from a maximum of 95 percent at Algoma (northwest of Sault Ste. Marie, Ontario) to minimum of 33 percent in Newfoundland. Averaged over the six monitoring sites, the U.S. contribution is approximately two thirds of the total airborne nitrate and nitric acid.

The Ontario Ministry of Environment (1986) has estimated the contribution of U.S. sources to sulphate and nitrate wet deposition at near border monitoring sites, using air parcel trajectory analysis. At least 80% of the sulphate and nitrate wet deposition in southwestern Ontario and 60% in southeastern Ontario is from U.S. emissions.

Table 10. Anthropogenic NO_x N deposition budget (kT nitrogen)*
(Shannon, 1986)

Source	Emissions	Dry		Wet		Total	
		U.S.	Canada	U.S.	Canada	U.S.	Canada
U.S.	6147	1706	108	1335	309	3041	417
Canada	555	65	146	25	85	90	231
Total	6702	1771	254	1360	394	3131	648

*Calculations are for 1980 emissions and 1976-1981 climatology.

Ozone

1. Greater Vancouver Regional District - Lower Fraser Valley

Concord Scientific Corporation (1982) has examined the meteorology of ozone episodes in lower mainland British Columbia for a four-year period (1978-1981). Five persistent episodes were identified during the four years and in each case the region was dominated by a stagnant anticyclonic weather system at the time of the episode. Meteorological conditions present in such systems promote local ozone formation. Southeasterly flow from the western U.S. occurred during several episode days. However, long-range transport of ozone or its precursors was not considered an important factor in the formation of ozone in the region. Elevated ozone concentrations in the Fraser River Delta were attributed to sources in the Greater Vancouver Regional District.

2. Southern Ontario

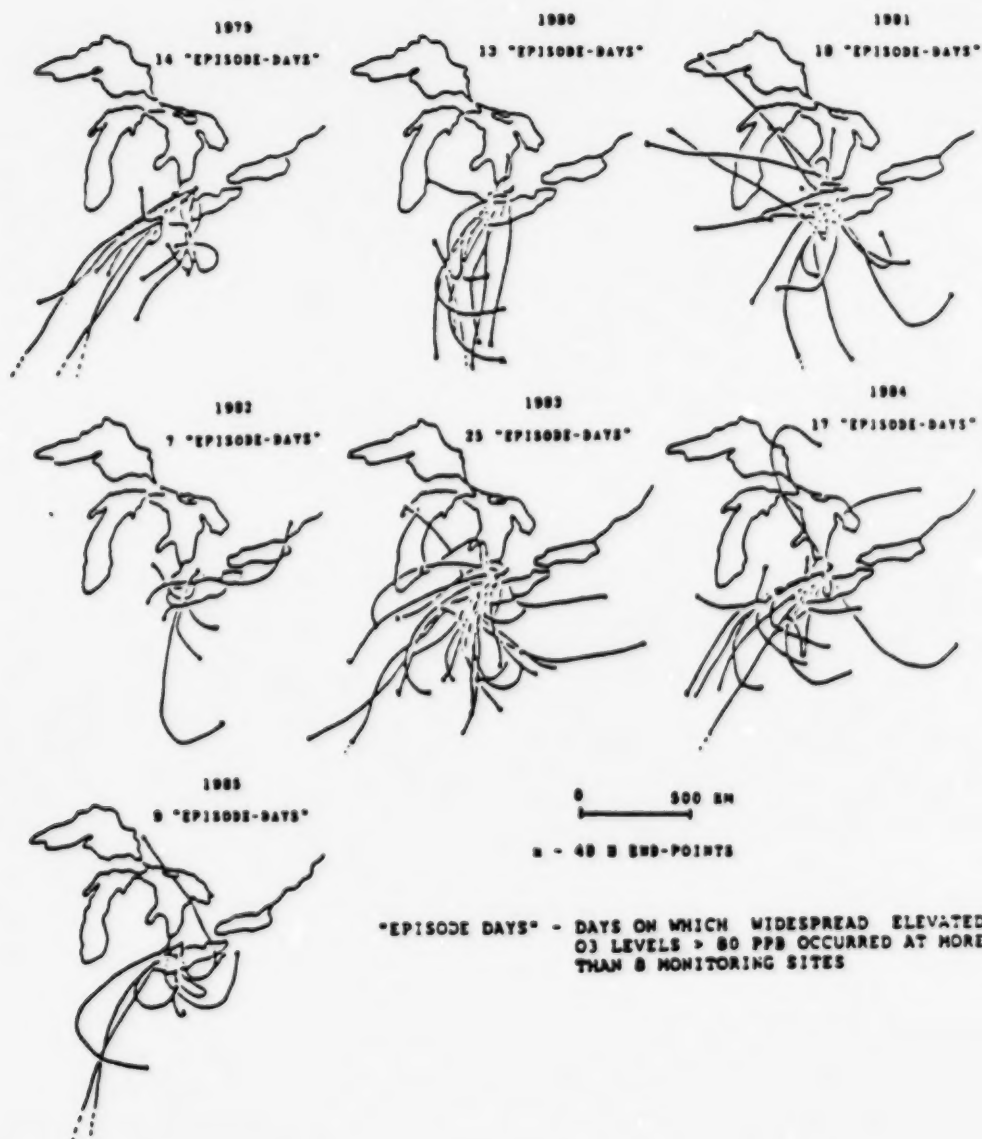
High ozone concentrations in southern Ontario are generally associated with southerly and southwesterly air flow from the backside of an anti-cyclone stagnant to the southeast (CSC, 1984). On some occasions a cyclonic system may be found north of the region. This synoptic situation brings ozone and its precursors from the industrial states to the south and west of the region. Trajectory analysis, using 48-hour back trajectories from a surface geostrophic model, further illustrates the importance of U.S. sources (see Figure 10). Yap et al. (1988) have estimated that 50-60 percent of the ozone in southern Ontario comes from U.S. sources. This estimate does not include ozone formed in southern Ontario from precursors originating in the U.S.

Local emissions contribute to elevated ozone concentrations downwind of Toronto and Sarnia. High ozone levels are often observed at suburban and rural monitoring stations outside of Metropolitan Toronto. The 1987 Growing Season Mean Ozone Concentration (0900-1600) at Stouffville, a town 35 km northeast of Toronto, was 41 ppb. The maximum 1-hour average concentration was 105 ppb and the maximum 7-hour average was 93 ppb (Dann, 1989). High ozone concentrations are usually associated with air arriving from the south or southwest which would have passed over Toronto. Yap and Chung (1977) have estimated that Toronto's contribution of ozone peaks at Stouffville is on average 30-40 ppb.

During the summer of 1984 the Ontario Ministry of the Environment carried out an intensive field study to determine the contribution of hydrocarbon and NO_x emissions from Sarnia to ozone concentrations in southwestern Ontario (Lusis, 1987). There is a concentration of petrochemical industries in the region. The study indicated that a measurable impact from Sarnia can be expected approximately 30 percent of the time during the summer months, particularly during sunny days with low wind speeds and reduced atmospheric mixing. Ozone concentrations attributable to Sarnia are of the order of 20-40 ppb (above the regional background level). The Sarnia contribution can result in occurrences of the 80 ppb standard. However, after consideration of the size of the area affected (approximately 1 percent of the total area of southern Ontario), the frequency of elevated ozone concentrations, and magnitude of the Sarnia contribution relative to regional background values, it was concluded that ozone concentrations in southern Ontario are primarily determined by U.S. sources.

FIGURE 10

48-h BACK TRAJECTORIES OF AIR PARCELS ON
'EPISODE - DAYS' IN SOUTHERN ONTARIO (YAP, 1988)



3. Montreal-Quebec City Corridor

Ozone measurements in the Montreal-Quebec City Corridor between 1979-1982 have been analyzed (CSC, 1983a). During the four year period, 16 areal episodes occurred in the Montreal region. Of these 16 episodes, 11 coincided with areal episodes in the state of New York, 10 coincided with episodes in Cornwall and three coincided with episodes in one of the two monitoring stations in Québec City. Twelve of the 16 episodes were associated with a common synoptic situation in which the St. Lawrence Valley was located in the north-west sector of an anti-cyclone, centered southeast of the Carolina or Virginia coast and in the warm sector of a cyclone centered over Hudson Bay, Northern Quebec and Labrador. Flow from the backside of the high was generally from the south west. This synoptic situation is very similar to that associated with ozone production in southern Ontario.

The long-range transport of ozone and its precursors makes a significant contribution to elevated ozone concentrations along the Montreal-Quebec City Corridor. Back-trajectory analysis (CSC, 1984) has identified two important trajectory corridors associated with episodes in Montreal. The first one passes over the industrial states of Indiana, Ohio and Michigan and southern Ontario. The second one passes over Pennsylvania and New York.

The Montreal-Quebec City Corridor is also influenced by the Montreal urban plume due to the quantity of ozone precursors emitted in Montreal and the channeling of airflow by the valley.

4. New Brunswick and Nova Scotia

Ozone data for 1978-1982 has been analyzed for New Brunswick and Nova Scotia (CSC, 1983b). Fourteen of the 17 episodes which occurred at sites in New Brunswick or Nova Scotia were associated with a synoptic pattern similar to that described for the Montreal-Quebec City episodes although the two systems were located further east. Surface air flow was from the southwest over the backside of the high.

Ozone levels in New Brunswick and Nova Scotia are significantly influenced by long-range transport. Eighty percent of the ozone readings over 82 ppb at the Canadian Forces Base Shearwater, Nova Scotia, occurred when winds were from the south or southwest (CSC, 1984). At Saint John, 19 percent were from the same directions.

A trajectory climatology method developed by Bottenheim et al (1988) suggests that ozone episodes at Kejimikujik (southwest, Nova Scotia) are associated with two distinct source regions. Ozone episodes at night originate mainly from the urbanized region of the United States east coast (see Figure 11). Day time episodes are associated with transport from upstate New York.



Figure 11 Envelopes of area containing the highest probability of trajectory residence in the 5 days prior to arrival at Kejimikujik National Park for the top 5% of the observed ozone mixing ratios (6 hourly averages). Unshaded for daytime; shaded for nighttime. (Bottenheim et. al. 1988)

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